PHOTOPHYSICAL CHARACTERIZATION OF NEWLY-SYNTHESIZED EMISSIVE MATERIALS

by
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ABSTRACT

RACHAEL ABIGAYLE NELSON: Photophysical Characterization of Newly-Synthesized Emissive Materials

(Under the direction of Dr. Nathan Hammer)

One key element in chemistry is understanding the chemical properties of a molecule so that its interactions with itself, other atoms or molecules, or its environment is well known. This knowledge alone allows the chemist to innovate and invent and thereby change the world. Light surrounds and sustains our lives; thus it is vital to understand how light interacts with common and newly synthesized materials. In this thesis the photophysical properties of newly synthesized materials will be discussed to give an overview of the many ways in which light interacts with the chemical materials composing our everyday lives. General photophysical phenomena will be discussed along with the spectroscopic devices and techniques used to explore said phenomena. The molecules to be discussed are Indolizine-Squaraine based dyes with potential use as a biological imaging dye, fac-tris(2-phenylpyridine) iridium(III) or Ir(ppy)3, and BisMethoxyMethylPhenyl BoraFluorene (BMMBBF) with potential use as an OLED (organic light emitting diode). The spectroscopic properties such as absorption, emission, fluorescent lifetime, stokes shift, quantum yield, molar absorptivity, and vibrational modes will be explored through the use UV-Vis-NIR, Raman, and IR spectroscopy. The molecules will be studied in the solid and solution state and environmental effects will be surveyed. The molecules studied were found to be appropriate for their desired purposes according to their photophysical properties.

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1. INTRODUCTION

A. Why physical chemistry is essential.

The studies of physical chemistry range from thermodynamics to quantum mechanics to spectroscopic analysis. One particular field of interest is photophysical characterization. This field is a culmination of the many facets of physical chemistry research and provides an avenue through which physical chemistry can be applied to all other areas of chemical research. Therefore, this skill and technique is an indispensable foundation to all future scientific discoveries.

To characterize a material of interest one must study the material at a molecular level. Certain questions must be asked and then answered with laboratory research. What bonds are present in the molecule? What are the intermolecular and intramolecular interactions? How does this molecule interact with light, extreme temperature, or various solvents? The curiosity needed to formulate and explore these questions leads to the identity and character of a molecule and indicates if it can be used for its intended purpose and what future possibilities exist.

To characterize molecules, multiple techniques and devices are utilized such as lasers, mass spectrometers, nuclear magnetic resonance, and electron microscopes[1]. Three spectrometers of interest when studying molecules are the Raman Spectrometer, Ultraviolent-Visible Spectrometer, and the Infrared Spectrometer. Each of these utilizes different wavelengths of light to determine the structure of molecules and their intermolecular interactions.

Some analytical techniques are absorption, emission, fluorescence lifetimes, single-molecule thin-films, diffuse reflectance, and quantum yield. By utilizing these techniques the specific properties of molecules can be studied. For example, if the desired use of a molecule is for medical imaging

dyes then it is important to know the absorbance and emission of the material. From these values the Stokes shift (difference between the maximum absorbance and maximum emittance wavelengths) can be calculated; a molecule with a large Stokes shift is more desirable because the laser used to excite will not interfere with the emission detection. In a material designed for solar cells a high fluorescence lifetime (time in nanoseconds that the molecule will remain excited) will allow the material to hold the energy from the incident light for a longer period of time. From this data one can determine if a particular molecule is suitable for its intended purpose. Therefore, using spectroscopic devices to determine the photophysical properties of compounds is the foundation for all future chemical discoveries and applications.

B. Molecular Motions

To characterize molecules using spectroscopy it is important to understand the effect that incident light has on the molecular motions. Photons of light contain energy that interacts with the material on which it is incident. Some of the energy will be absorbed by the molecules and energy at a specific wavelength will be reflected producing the color observed. The energy, when absorbed, may also cause excitation of the different energy levels within the molecule such as translational, rotational, vibrational, and electronic. Translational energy refers to the shift of a molecule from one position to another. Rotational refers to the turning or spinning of the molecule. Vibrational energy describes the ways in which the bonds between the atoms can behave. A vibration in a molecule is the motion that two atoms make in relation to each through the covalent bonds. Usually vibrations are studied in relation to the central atom. When energy is absorbed the atoms themselves can move in different ways: in a bending motion moving closer or farther from each other, in a symmetric stretching motion moving in and out from the central atom at the same time, and in an asymmetric stretching motion moving in and out from the central atom at different times. These and molecular vibrations are illustrated in Figure 1.

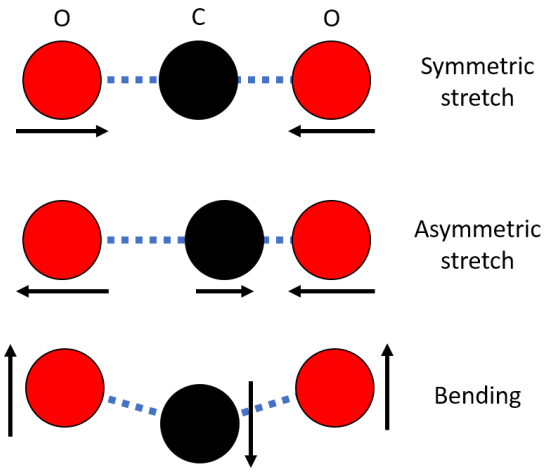

Figure 1: Common molecular vibrations for CO_2. (Adapted from reference 2)

These vibrational energy motions are referred to as vibrational modes and correspond to wavelengths specific for each molecule. Electronic energy levels refer to the transition of an electron in a molecule to an excited state above the ground state. These energy shifts are described by a potential energy curve as pictured in Figure 2, and they can be detected using spectroscopic devices.

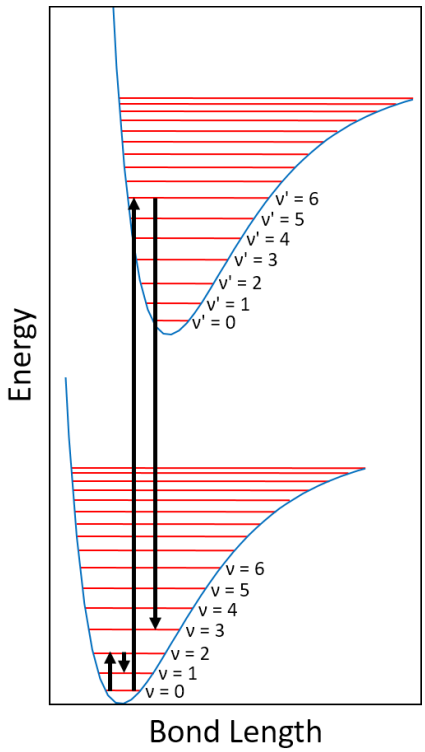

Figure 2: Potential energy curve illustrating electronic and vibrational transitions.

To study these different molecular motions several different spectroscopic instruments have been invented. Each technique uses a different region of the electromagnetic spectrum to excite different transitions within the molecule and observe different photophysical phenomena. Figure 3 displays an electromagnetic spectrum with emphasis on the region spectroscopically studied most.

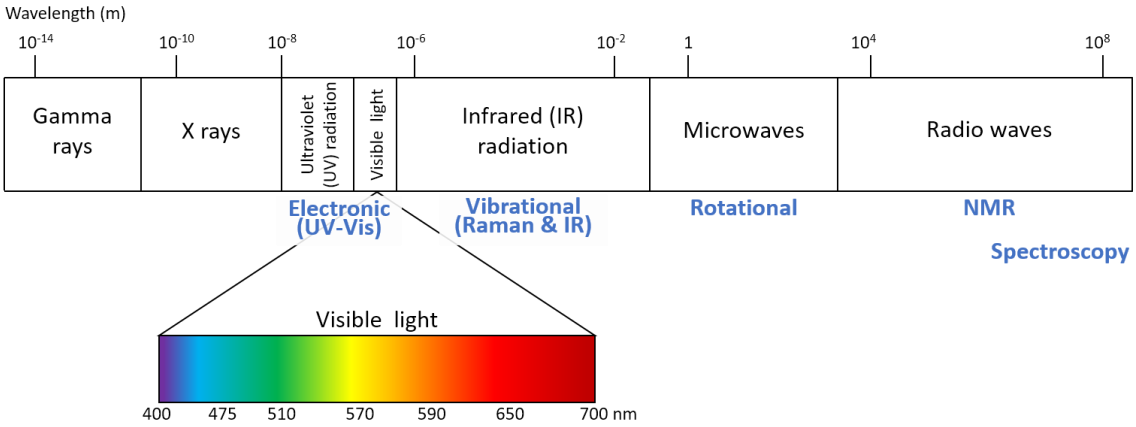

Figure 3: Electromagnetic spectrum with spectroscopy to detect each molecular motion indicated. (Adapted from reference 3)

C. Spectroscopic Methods

a. Devices

i. Raman Spectroscopy

Raman Spectroscopy is one specific spectroscopic technique that utilizes light in the ultraviolet, visible, and near infrared wavelengths to determine the structure and composition of molecules. A molecule's Raman spectrum, in conjunction with the IR spectrum, can be used to characterize the molecule and compare it to other known molecules.

The number of modes, or motions, for a molecule can be described using degrees of freedom. A degree of freedom is the number of variables necessary to describe the location of an atom in space. For a single atom three coordinates are used, similar to the x, y, and z Cartesian coordinates. When the atom "translates" to a different location these terms indicate its new

location. Therefore, for a molecule of N atoms the number of translations is equal to 3N, corresponding to the three coordinates. However, since all the atoms cannot move independently there will only be three translational modes and three rotational modes, about the three axes, for one molecule; the remaining modes are vibrational. There are 3N-6 vibrational modes for a non-linear molecule (3N = total number of modes; 6 = 3 translational + 3 rotational). For linear molecules there are 3N-5 vibrational modes (total modes – 3 translational – 2 rotational); this is because there are only two noticeable rotational motions (the third rotation is on the axis of the molecule and does not give a different location).

Raman spectroscopy is useful because it can detect the inelastic scattering in vibrational, rotational, or electronic energy levels produced by incident light.[4] The steps for detection with Raman spectroscopy are as follows. Firstly, the molecule of interest is put in solution or kept in the solid-state and laser light is incident. Next, the atoms and bonds within the molecule absorb the energy and the molecular energy is raised to a virtual excited state. This state is lower in energy than a complete electronic transition. This excited state is unstable, so the molecule will relax to the ground, or initial, state or to a state of higher or lower energy than the ground state. This relaxation is termed scattering. Most of the relaxing photons will elastically scatter to the ground state, known as Rayleigh scattering. A few photons will be inelastically scattered to a state of higher energy, known as Stokes scattering. Even fewer photons will inelastically scatter to a state of lower energy, known as anti-Stokes scattering. These transitions are illustrated in Figure 4.

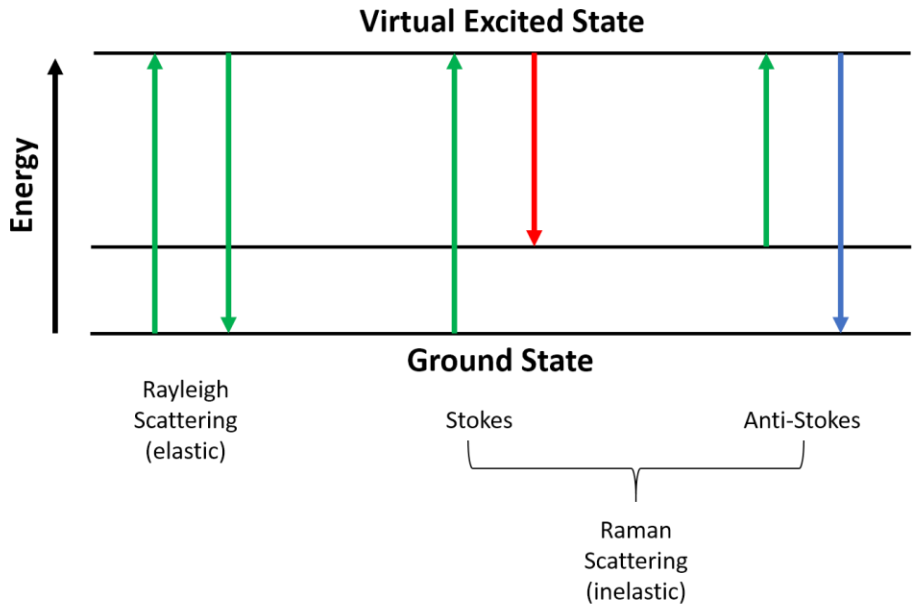

Figure 4: Raman (Stokes and anti-Stokes) and Rayleigh scattering. (Adapted from reference 5)

Inelastic scattering is referred to as the Raman effect, and it is hard to detect past the signal from the Rayleigh scattering; therefore, a high signal is needed and a sensitive device such as the Raman spectrometer is used. Blue and green laser light is useful for inorganic materials and surface enhanced Raman scattering (SERS), red and near infra-red for fluorescence suppression, and ultraviolet for bio-molecules and fluorescence suppression[6].

ii. Infrared Spectroscopy

Light in the infrared (IR) region (700 nm to 1000000 nm or 1 mm) is of lower energy than that in the ultraviolet and visible regions; therefore, it excites the vibrational and rotational motions of a molecule rather than the electronic. For ease of analysis the wavelength measurements are converted to wavenumbers (cm^{-1}) and are measured from 12800 cm^{-1} to 10 cm^{-1}. When light waves interact with a molecule if the frequency of the light is the same as the frequency of the molecular vibration a peak will appear on the IR spectrum. Since each vibrational mode will correspond to a bond within the molecule, the structure of the molecule can be determined. The key with IR spectroscopy is that the molecule must have a change in the dipole

moment. If this is not present the molecule is not “IR active,” and an IR spectrum cannot be collected. For this reason, vibrational modes that cannot be determined with IR spectroscopy can be seen with Raman analysis. As with Raman spectroscopy the number of vibrational modes expected is given by 3N-5 for linear molecules and 3N-6 for nonlinear molecules.

iii. Ultraviolent/Visible spectroscopy

In the study of molecules, determining the absorption range of the molecule is vital so that the potential uses of the material can be specified. Absorption occurs when light energy from photons is taken in by the molecules and converted to kinetic energy as electrons move to higher states of excitation. All of the energy from the light is absorbed, but certain wavelengths cause excitation in the electronic energy levels. These levels can then relax through fluorescence which will be discussed later. Ultraviolent and visible light in the wavelengths 100 nm to 700 nm causes excitation in the electronic energy levels. Within each electronic transition there are also vibrational and rotational transition. This absorption of energy can be detected by ultraviolet/visible absorption spectrometry (UV/Vis) by using a CCD camera. A charged-coupled device (CCD) camera detects the photons of incoming light from the sample and converts it to electrical charge to create a spectroscopic spectrum. Figure 5 shows a typical set-up for a UV-Vis spectrometer.

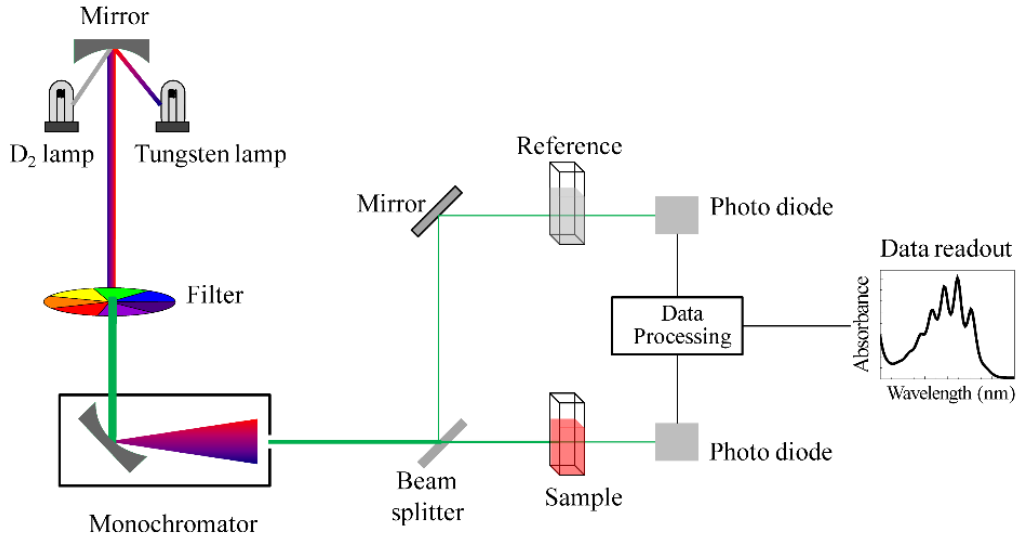

Figure 5: Ultraviolet-visible spectrometer schematic. (Used with permission from reference 7)

b. Analysis:

i. Absorption

The absorbance spectrum for each molecule of interest can be collected in the solution or solid state by two different techniques. For the solution state an appropriate solvent is chosen and the molecule of interest is dissolved to create a molarity to the order of 10^{-4} to 10^{-5}. This solution is then placed in a glass or quartz cuvette and analyzed with a UV-Vis spectrometer.

For solid-state analysis the crystals of the sample are placed between two glass slides and the absorbance spectrum is collected through a technique termed diffuse reflectance. As displayed in Figure 6, irradiation from a Xenon lamp is carried to an integrating sphere through a fiber optic cable. A second fiber optic cable carries the light exiting the integrating sphere to a detector. The detector sends the information to a computer that will display the absorbance spectrum.

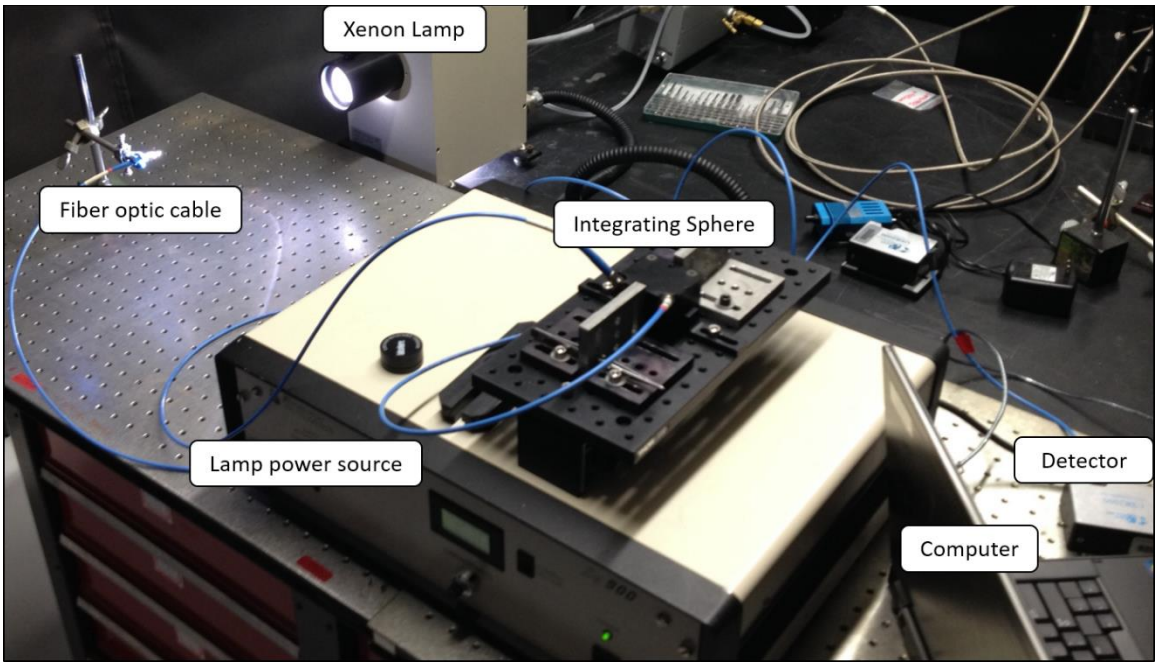

Figure 6: Diffuse reflectance experimental set-up.

The integrating sphere is a box with a hollow, white interior in the shape of a sphere. The white interior will reflect all incident light and therefore create a spectrum of zero absorbance; this will serve as the blank. When the sample is placed in the integrating sphere there will be reflection and absorbance of the incident light; the sample will reflect the wavelengths of light corresponding to the visible color observed, and the other wavelengths will be absorbed. The detector will record the change in reflectance, and from this data the computer will generate an absorbance spectrum.

From the absorbance spectrum the molar absorptivity of the molecule can be determined. This is a measure of how well the molecule will absorb incident light, and can be calculated with the Beer-Lambert law (Equation 1) in which *A* is the absorbance, ε is the molar absorptivity, *b* is the distance the light travels through the solution (or the cuvette width), and *c* is the concentration of the solution. Since this equation includes the concentration the values for various solutions can be easily compared.

$$A = \varepsilon bc \quad (1)$$

ii. Emission

After the absorbance maximum is determined for a molecule of interest using UV-Vis absorption spectroscopy that specific wavelength of light is isolated and used to excite the sample. First the laser being used is set to only irradiate a specific wavelength. Then the light passes through a series of filters to further isolate the desired wavelength. Mirrors are used to direct the light to the sample, and the light emitted by the sample enters the CCD camera and creates an emission spectrum. This experimental set-up is shown in Figure 7. Since the wavelength that causes maximum absorption is used, it is expected that the observed emission will be at the maximum amount.

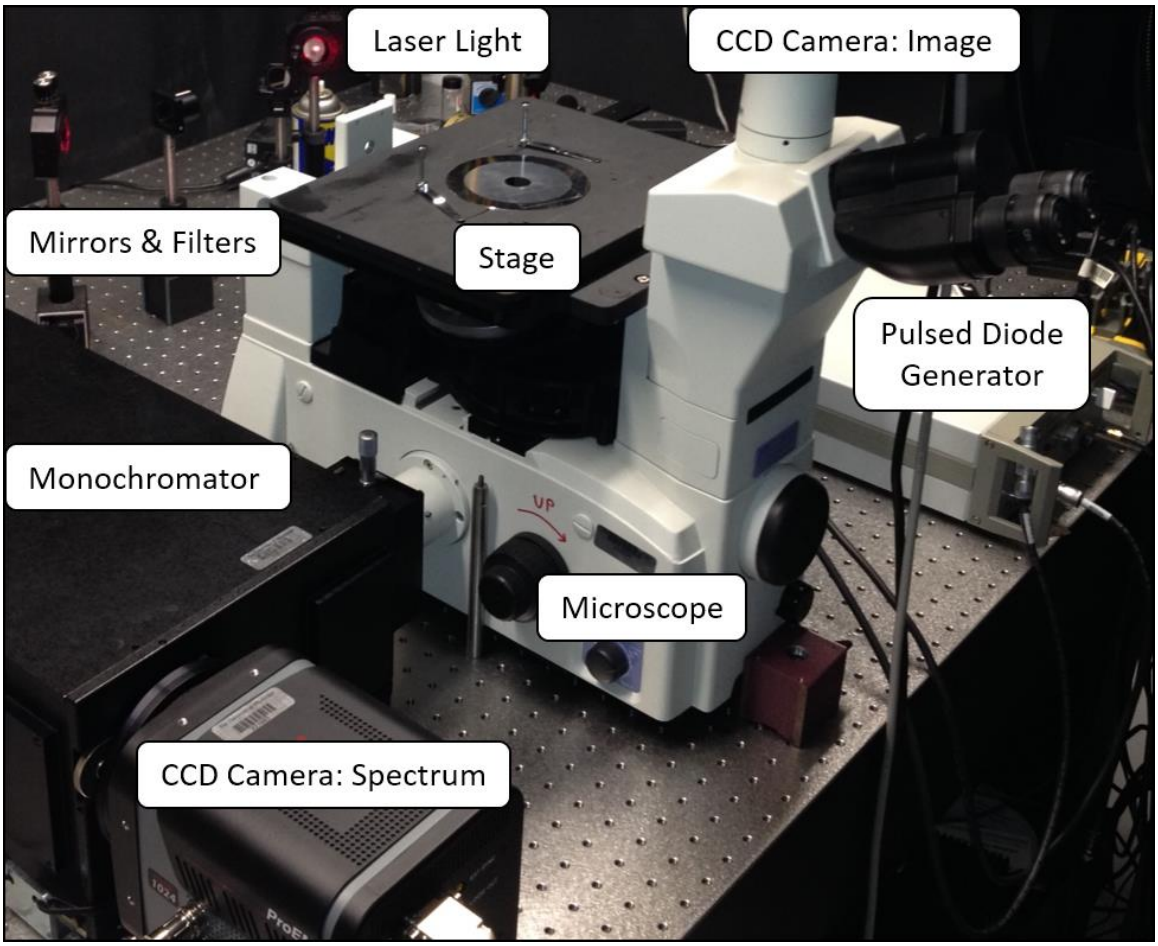

Figure 7: Emission and fluorescent lifetime experimental set-up.

The emission spectrum of samples can be collected in both the solution and solid state for molecules in bulk and in a single-molecule thin-film. The reason for these different sample states will be discussed later in the solvent effects section. The same solution used for absorbance analysis can be used to determine the emission. For solid-state analysis, a few crystals of the dry sample are placed on a glass slide and the laser is focused on the sample.

To create a single-molecule thin-film a dilute solution of the solid in cyclohexane is made. If dissolution in cyclohexane does not occur, the solid is first dissolved in dichloromethane or chloroform; this solution is this diluted with cyclohexane. Then Zeonex polymer pellets are added and the solution is heated and sonicated. A few drops are placed on a glass slide and a smooth, thin film is created over the glass. After the film dries it is placed on the microscope stage. The microscope is focused on one molecule of the solid within the thin-film, and an emission spectrum at this spot is collected. The term single-molecule is used to refer to the laser focusing on one molecule. The term thin-film refers to the polymer solution being so dilute that the thin layer applied to the slide is theoretically one molecule thick.

From the recorded emission spectrum several characteristics of the molecule can be studied such as stokes shift, quantum yield, and fluorescence lifetime. Stokes shift is simply the difference between the maximum absorption and maximum emission wavelengths. A high Stokes shift is a vital characteristic for many materials such as those designed to be used as imaging dyes because it ensures that the light used to excite the material will not interfere with and be mistaken for the emitted light.

Quantum yield is a calculation of interest to determine the efficiency of a sample to emit the absorbed light.[8] The technical definition of this measurement is the fraction of molecules that emit a photon after direct excitation by the source[9]. This value is usually close to the ratio of the number of emitted photons to the number of absorbed photons. This latter definition is the one

commonly used. To calculate the fluorescence quantum yield, or quantum efficiency, the formula displayed in Equation 2 is used in which *Q* is the fluorescence quantum yield, *a* is the absorbance at the excitation wavelength, *A* is the area under the fluorescence spectrum, and *n* is the refractive index; *sam* and *ref* refer to the values for the sample and reference materials respectively.[8]

$$Q_{sam} = Q_{ref} \times \frac{a_{ref}}{a_{sam}} \times \frac{A_{sam}}{A_{ref}} \times \left(\frac{n_{sam}}{n_{ref}}\right)^2 \quad (2)$$

Fluorescence lifetime tells how long the electrons remain in the excited-state until the energy is emitted. To determine this a pulsed-diode laser of a single wavelength is used. The pulsed diode generator (shown in Figure 7) will rapidly turn the laser on and off to excite the electrons within the molecule, thus, allowing a period of rest. During this "rest period" the electrons emit the absorbed photons and the time of this transition from excited to ground state is recorded as the fluorescent lifetime.

To detect the fluorescence signal from the sample each emitted photon is considered independently by a technique termed Time-Correlated Single Photon Counting (TCSPC)[10]. This technique records the release of single photons relative to their detection time with a picosecond time resolution[11]. A single photon avalanche diode detector is used to perform the TCSPC; this counts the number of output pulses (to give intensity) and creates a time-dependent waveform.

The lifetime, indicated by τ, can be calculated with Equation 3 in which *y* is the measure of the peak intensity at a specific time *x*, y_0 is the initial intensity, x_0 is the initial time, and *A* is the amplitude of the decay curve. The lifetime can also be approximated by the measurement of the full width of the peak at half of the peak's maximum termed full-width half-max (FWHM). A longer lifetime indicates that the molecule is more stable in the excited state and therefore has more potential to be used for fluorescent purposes.

$$y = y_0 + Ae^{-\left(\frac{x-x_0}{\tau}\right)} \quad (3)$$

D. Environmental effects

a. Solvent Effects

As seen from all chemical reactions, molecules exhibit different properties when they are in the presence of other molecules or atoms. This concept extends into the effects that a solvent has on chemical properties such as solubility, polarity, stability, boiling point, and reaction rate. The changes in these properties are then reflected by changes in the spectroscopic properties such as maximum absorption wavelength and intensity; the effect that the solvent can have on a chemical's color and therefore spectroscopic properties is termed solvatochromism. For example, with an increase in the polarity of a solvent there is a hypsochromic shift, or blue-shift, to shorter wavelength for the absorption maximum of nonpolar aromatic hydrocarbons.[12] Conversely, increased solvent polarity will cause polar fluorophores to emit at longer wavelengths (bathochromic or red-shift) but will have only a small effect on the emission of nonpolar aromatic hydrocarbons.[13]

From the above phenomena a general rule of solvatochromism can be illustrated. When a nonpolar molecule is dissolved in solvents of increasing polarity there will be less molecule-solvent interaction; this will increase the energy within the molecule. Due to the inverse relationship between energy or frequency of light and the corresponding wavelength, this increased energy will be spectroscopically reflected with a shorter (lower nm value) wavelength. Conversely, for a polar molecule, increased polarity of the solvent will increase the amount of molecule-solvent interaction resulting in a lower energy and longer (higher) wavelength.

If there is an increase or decrease in the wavelength of the absorbance curve then it can be concluded that the molecule-solvent interaction occurs predominantly in the ground state; thus a change in the ground state geometry occurred. On the other hand, if the change in wavelength occurs in the emission curve then there was a change in the excited state geometry.

Thus, two general rules can be elucidated: 1) a change in the energy/wavelength indicates a change in the degree of geometric interaction and 2) the state effected (ground or excited) will be indicated by the curve effected (absorption or emission).

i. Liquid

When choosing a solvent for spectroscopic analysis it is important to consider the intended purpose, solubility, and polarity of the molecule of interest. For example, it is advantageous that molecules synthesized for use in biological systems be either soluble in water or a polar solvent. Whereas molecules for flexible solar cells or organic light emitting diodes (OLEDs) must dissolve in solvents that are safe to use in mass production. In the case of synthesized biochemical molecules, water dissolution is ideal; however, if this is not possible a different polar solvent will be used for spectroscopic study to give the general properties. From these results the synthetic chemist will know how to modify the molecule for both improved spectroscopic properties and increased polarity. As discussed earlier, if an absorbance or emission in a specific range or "window" of wavelengths is desired either the solvent could be change to increase or decrease the wavelength or the molecule could be modified to change the molecule-solvent interactions.

It is also important to be aware of the solution molarity when completing spectroscopic analysis because intermolecular interactions can influence or quench the emission signal from the individual molecules. For this reason, a low solution concentration is used (on the order of 10^{-4} or 10^{-5}) and analysis in the solid and single-molecule states are carried out as detailed below.

ii. Gas

Just as the solvent used impacts the spectroscopic properties of a molecule so, the gaseous environment surrounding the solution has an effect. Gas can be bubbled through the solution and fill the headspace of the container of the material to be analyzed. Common gases

used to study these effects are air, nitrogen, and carbon dioxide. The objective in changing the gas is to remove any oxygen or water in the environment because these can cause quenching in the fluorescence lifetimes. Thus, with a nitrogen environment, for example, an increase in the fluorescent lifetime would be expected when compared to the lifetime in ambient air.

iii. Sample state

Due to the effect that both solution and environment can have on photophysical properties most spectroscopic studies are carried out with molecules in the solid and solution state as well as in a single-molecule thin-film. As discussed earlier, the molecule-solution and intermolecular interactions will affect how and where the molecule absorbs and emits light. To prevent this interaction, analysis is completed in the solid state. To ensure that there is no influence on the spectroscopic properties the sample is dispersed in a single-molecule thin-film. The Zeonex polymer used should have no interaction with the molecules, so the collected emission spectrum or fluorescence lifetime will be solely from the molecule of interest.

b. Pressure and Temperature

Other environmental factors can affect the spectroscopic properties of synthesized molecules such as pressure and temperature. A vacuum pump can be used to change the pressure. With an increase in pressure there will be a blue-shift to lower wavelength; likewise, a decrease in pressure will produce a red-shift. To change the pressure of the system an experimental set-up as depicted in Figure 8 is used.

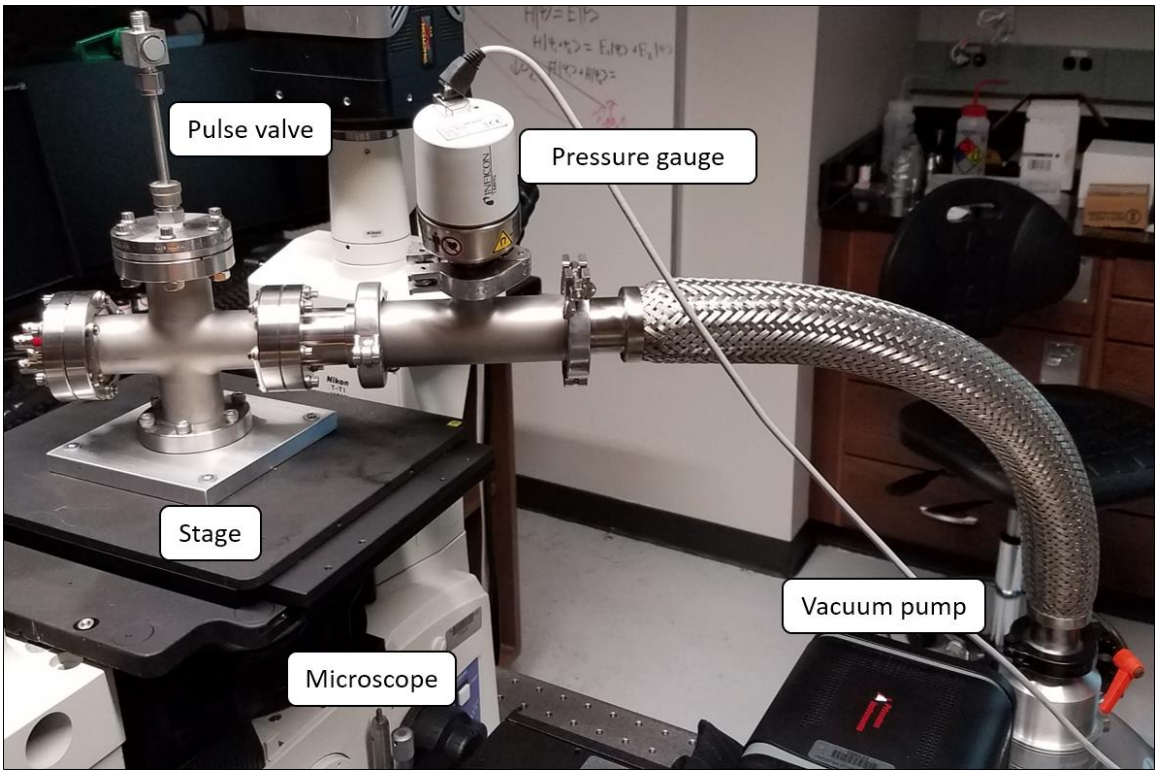

Figure 8: Vacuum pump experimental setup.

To decrease the temperature of the molecules to be analyzed liquid nitrogen can be used to surround the solution. With a decrease in temperature there will be a blue-shift. In Raman spectroscopy there is a specific method developed named Raman under liquid nitrogen (RUN) that utilizes the consequential decrease in temperature. Molecular motions will slow with lower temperature thus revealing more vibrational modes in the Raman spectrum.

2. APPLICATIONS OF PHOTOPHYSICAL CHARACTERIZATION

A. Overview of molecules

To understand the effect that environment can have on spectroscopic results several molecules were studied. The photophysical properties of these molecules were characterized in regard to absorbance, emission, fluorescence lifetime, quantum yield, and Raman Spectroscopy. Studies were conducted in the solid and solution phase to examine the intermolecular interactions. The molecules of interest were synthesized for specific purposes; thus, the suitability of the molecule for its purpose was determined by the photophysical properties. The newly-synthesized molecules that will be discussed are summarized in Table 1.

Table 1: Newly synthesized emissive materials spectroscopically studied. The symbols ε, Φ, and τ indicate molar absorptivity, quantum efficiency, and fluorescence lifetime respectively.

Molecule	Abbreviation	Intended purpose	Properties Studied
Indolizine-Squaraine	In-SQ	Medical imaging dyes	Abs., Emis., ε, Φ, τ
fac-tris(2-phenylpyridine) iridium(III)	$Ir(ppy)_3$	Catalyst, OLEDs	τ
BisMethoxyMethylPhenyl BoraFluorene	BMMBBF	OLEDs	Abs., Emis., Raman

B. Findings for each molecule

a. Indolizine-Squaraines

General structure, properties, applications

The first set of molecules to be discussed are the Indolizine-Squaraine molecules. These molecules emit in the near infrared (NIR) region and are molecularly engineered to have an increased Stokes Shift. The base of the molecule is squaraine and it has been used in biological

imaging dyes. Through recent advancements in medical diagnosis the demand for improved medical imaging dyes have increased. For higher resolution biological imaging several chemical qualities are important namely 1) water solubility, 2) absorbance and emittance in the therapeutic window (700 nm-1400 nm), and 3) large Stokes shifts (large difference between absorbance and emittance maxima).

The current NIR indoline-squaraine dyes fall short of these qualities; however, the squaraine base remains a vital feature of the molecule due to the low molecular weight and concise synthesis. Thus, the indoline donor group was replaced by an indolizine group. This substitution creates steric hindrance, which increases the Stokes shift and improves the water solubility (Figure 9). To this indolizine-squaraine-indolizine (In_2SQ) base twelve different substituents were added to study the tunability of the chemical properties of this new class of material. The In_2SQ base along with the twelve substituents are pictured in Figure 10.

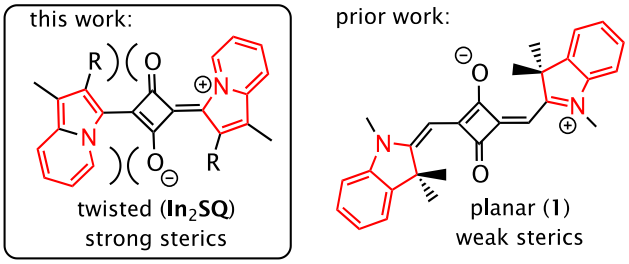

Figure 9: Indolizine-squaraine structure being studied compared to the previous indoline-squaraine base. The electron donor is in red.[14]

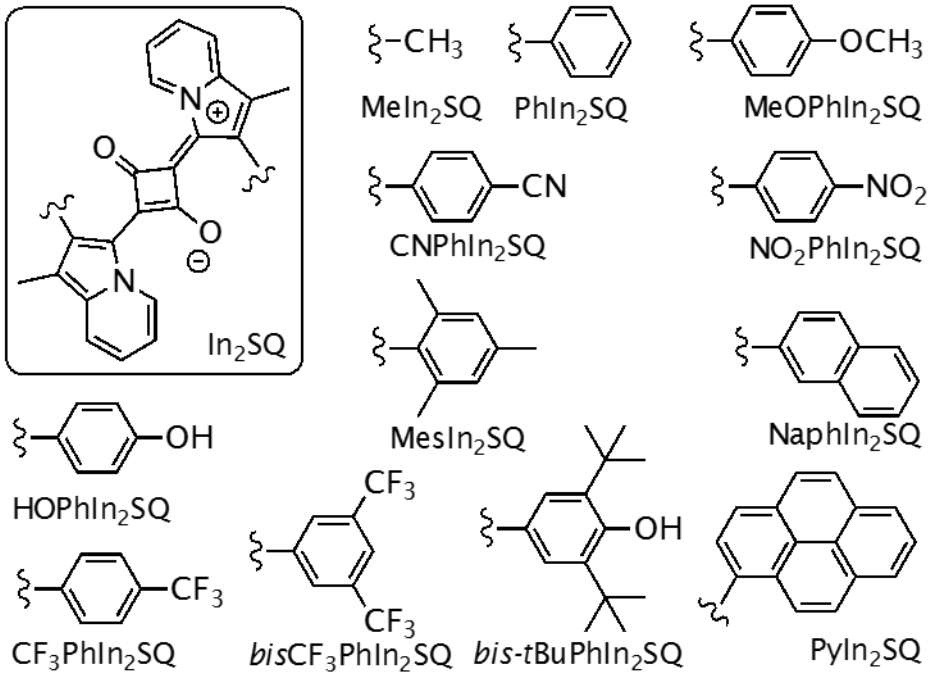

Figure 10: Indolizine-squaraine-indolizine base with the twelve different substituents used to survey the tunability.[14]

To quantify its effectiveness for medical dyes the photophysical properties such as Stokes shift, molar absorptivity, quantum yield, and fluorescence lifetime were assessed. A large Stokes shift is desirable because it prevents light source interference with the detector. If the molar absorptivity is high it shows that the molecule can absorb light well; whereas, a high quantum yield (or quantum efficiency) indicates that the molecule will emit light effectively thereby providing a high image resolution. Fluorescence lifetime values show how stable the excited state is, so a high lifetime is desirable to provide higher image resolution.

Experimental techniques and instruments

The spectroscopic properties of the indolizine-squaraine molecules were studied in the solution and solid state in the ultraviolet-visible-near infrared range. Solutions were made with dichloromethane (DCM) and toluene for the indolizine-squaraine base with its twelve substituents and for an indoline-squaraine standard (indicated by (1) in figures). Figure 11 shows

the solutions for the standard and Figure 12 shows molar dilutions in DCM to 10^{-4} and 10^{-5} for the substituted In_2SQ.

Figure 11: Indoline-Squaraine standard solutions in DCM (1 X 10^{-5} M) at left and toluene (1 X 10^{-4} M) at right.

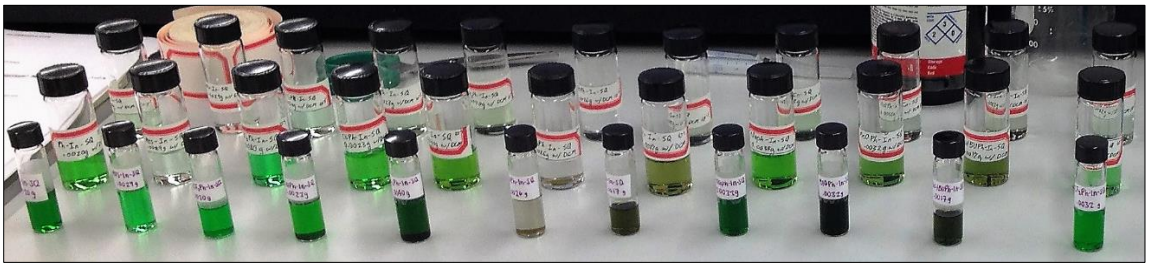

Figure 12: Molar dilutions of In_2SQ based substituents in DCM to 1 X 10^{-4} M and 1 X 10^{-5} M.

For absorption analysis of the indoline and indolizine solutions a Cary 5000 UV-Vis-NIR spectrometer was used. Indoline-squaraine in DCM and Toluene was analyzed as a standard to give maximum absorption at 630 and 640 nm respectively. Solid state absorbance was completed using diffuse reflectance spectroscopy with an Ocean Optics detector.

To evaluate the emission in the solution and solid state a Coherent Innova 200 Krypton-Argon ion laser at red laser light of 647 nm was used in conjunction with a 647 nm laser-line filter, two long-pass filters at 650 and 660 nm, and a ND30 (neutral density) filter to block 99.9% of the laser power. A Nikon Eclipse TE 2000-U inverted microscope and a Photon Max 512 CCD camera was used to detect the emission signal from the sample. The emission spectrum was collected from 740 nm to 880 nm at 70 nm increments, and the spectra were combined and normalized using Microsoft Excel and Igor graphing software. Zinc phthalocyanine dye was used as a standard;

the background was collected for the microscope with nothing on the stage. For fluorescence lifetimes the same Krypton-Argon ion laser was used at 485 nm in conjunction with a 485 nm line filter (instead of the 647 nm line filter) along with all of the previous filters detailed earlier.

Analysis using Raman spectroscopy was attempted, but a spectrum with clear peaks was not produced. Therefore, analysis was completed using ATR-IR (attenuated total reflection) to determine which conformational isomer was produced from the synthetic reaction. The modes of the isomers were determined and compared to those produced from a computational IR spectrum of both the cis and trans forms. The difference in the IR spectra is only noticed in the 1600 to 1800 cm^{-1} region which revealed more agreement with the cis computational spectrum; thus it was confirmed that the cis isomer was produced in the synthesis.

The Raman spectrometer was used, however, to collect an image of the solid-state emission and assess the potential of the molecule to be used as an organic light-emitting diodes (OLEDs) in the NIR region. Crystals of $PhIn_2SQ$ were arranged on a glass slide in the shape of an "M" and covered with white filter paper. When visible light was used as an illumination source no emission signal was present; however, when NIR light at 785 nm was used an emission at 850 nm was visible through the white filter.

Results and Discussion

The absorbance spectra for the solution and solid state are displayed below. Figure 13 gives the spectra for the indoline-squaraine standard in DCM and toluene. The absorption and emission maxima in toluene along with the calculated stokes shift, molar absorptivities, quantum yield, and fluorescent lifetimes are displayed in Table 2. The molar absorptivities were calculated using the absorbance values in DCM, and they are graphically compared in Figure 14. The theoretical IR spectra for the cis and trans form of the conformational isomer are pictured in

Figure 15 in comparison to the experimental ATR-IR spectra. The image produced by the Raman spectrometer by solid state emission of $PhIn_2SQ$ is displayed in Figure 16.

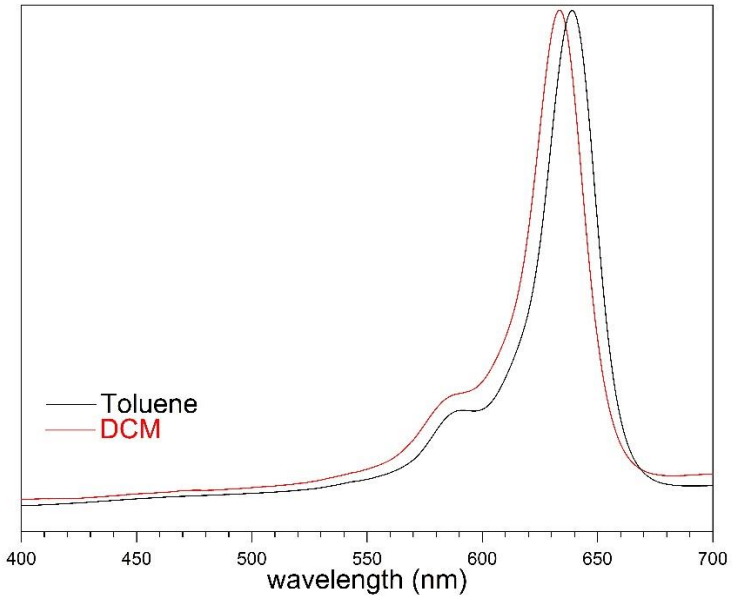

Figure 13: Absorbance spectrum for indoline-squaraine standard in DCM (red) and toluene (black).

Table 2: Absorption, emission, stokes shift, molar absorptivity, quantum yield, and fluorescent lifetime of indolizine-squaraine based dyes and indoline-squaraine standard (1) in toluene. *$HOPhIn_2SQ$ was dissolved in DMSO.

Dye	Absorption Max. (nm)	Emission Max. (nm)	Stokes Shift (nm, eV)	ε ($M^{-1}cm^{-1}$)	Φ (%)	τ (ns)
$MeIn_2SQ$	712	738	26, 0.055	210,000	8.9	0.42
$PhIn_2SQ$	723	756	33, 0.075	181,000	3.7	0.45
$NaphIn_2SQ$	727	766	39, 0.087	150,000	5.3	0.45
$PyIn_2SQ$	729	757	28, 0.063	124, 000	10.5	1.11
$PyIn_2SQ$ (trans)	730	756	26, 0.058	160,000	5.8	1.03
$PyIn_2SQ$ (cis)	730	754	24, 0.054	110,000	12.1	1.46
$MesIn_2SQ$	724	735	11, 0.026	262,000	7.3	0.30
***Bis*-*t*BuPhIn_2SQ**	722	770	48, 0.107	216,000	6.7	0.55
***Bis*-CF_3PhIn_2SQ**	727	757	30, 0.068	260,000	12.0	0.79
CF_3PhIn_2SQ	727	765	38, 0.085	166,000	5.9	0.40
$CNPhIn_2SQ$	729	756	54, 0.119	213,000	5.8	0.65
NO_2PhIn_2SQ	732	769	37, 0.082	185,000	11.2	0.65
$MeOPhIn_2SQ$	723	761	38, 0.086	140,000	4.5	0.33
$HOPhIn_2SQ$	723*	756*	33, 0.075*	185,000*	1.0*	0.09*
1	633	653	20, 0.050	229,000	16.0	2.40

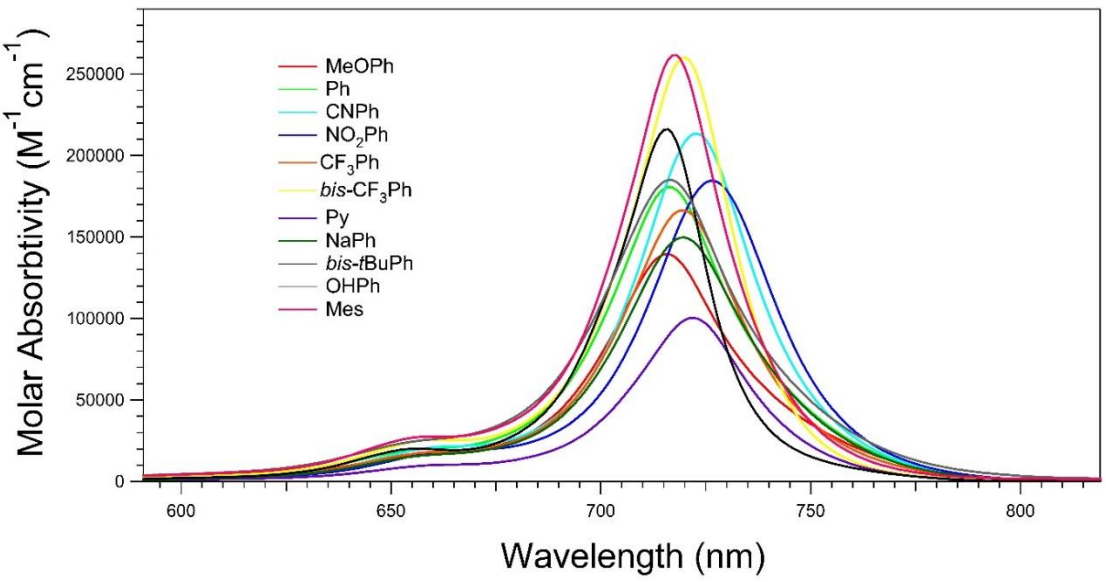

Figure 14: Molar absorptivities of all dyes in DCM.

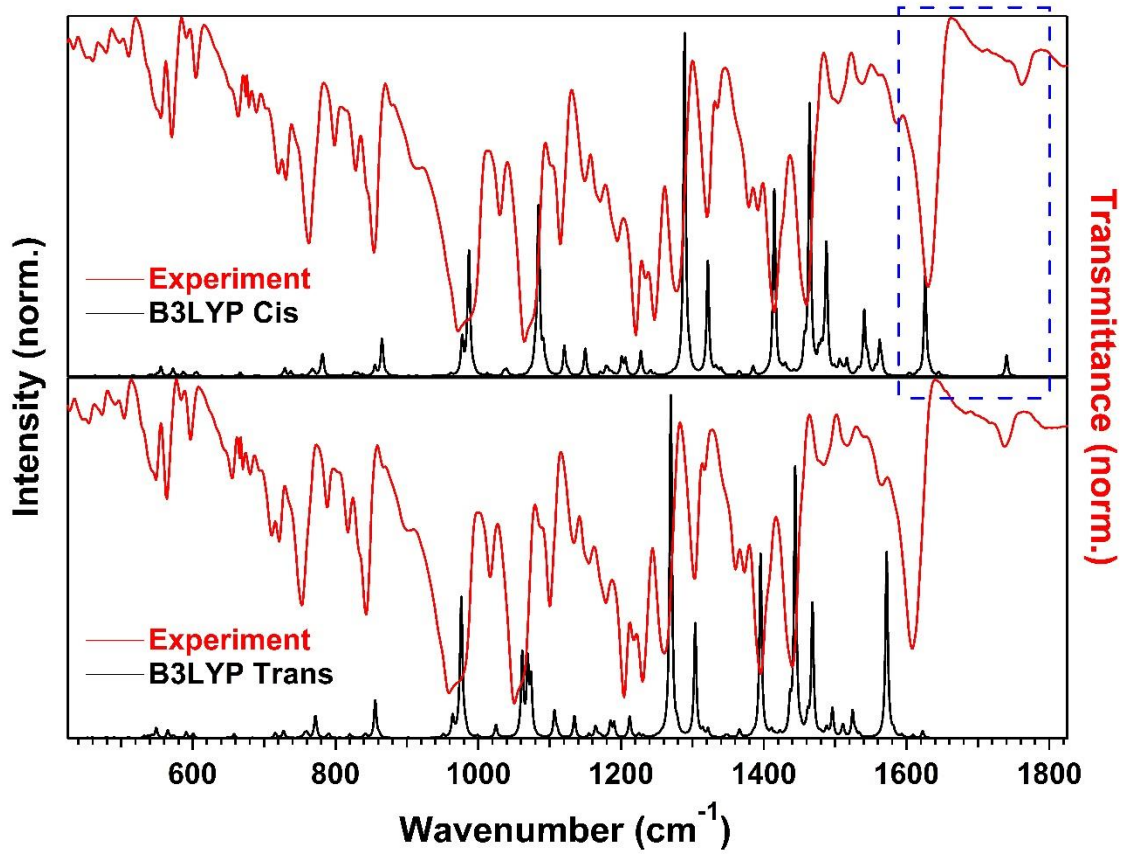

Figure 15: Theoretical IR (black) cis (top) and trans (bottom) spectra and experimental ATR-IR (red) spectra comparison for $PhIn_2SQ$.

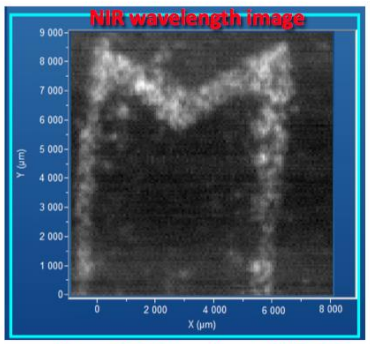

Figure 16: NIR image of $PhIn_2SQ$ collected with the Raman spectrometer.

Suitability for proposed application

Spectroscopic analysis reveals emission maxima from 730 to 770 nm and absorbance maxima from 712 to 730; these are well within the therapeutic window and red-shifted when compared to the indoline-squaraine standard. The maximum Stokes shift of 54 nm prevents interference of the absorbance signal with the detector, and the maximum quantum yield of 12.1% shows that the molecules can effectively emit the absorbed light. The maximum fluorescence lifetime of 1.11 ns indicates a stable electron excited state which, in turn, shows that the molecule will hold the energy efficiently and provide a strong signal. Overall, this novel class of NIR emitting molecules shows significant improvements from the indoline-squaraine based molecules in increased Stokes shift, improved water solubility, and high quantum yields. Therefore, the indolizine-squaraines are a great candidate for medical imaging dyes. The molecule's ability to emit in the solid state demonstrates its suitability for potential OLED purposes.

b. $Ir(ppy)_3$

General structure, properties, applications

Although the fac-tris(2-phenylpyridine) iridium(III), $Ir(ppy)_3$, molecule is not newly synthesized it was spectroscopically studied to reveal the effect of environment on fluorescent lifetime values. The structure is given in Figure 17.

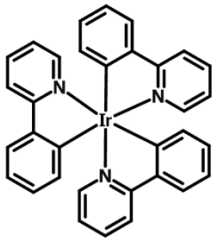

Figure 17: Molecular structure of $Ir(ppy)_3$.[15]

Experimental techniques and instruments

The fluorescent lifetimes of $Ir(ppy)_3$ base with three different substituents, -BIH, -$Co(CNC)_2$, and –$Fe(CNC)_2$, were studied under air, nitrogen gas, and carbon dioxide gas. A 405 nm pulsed diode laser light was used for excitation. The spectra collected for air (Figure 18) and CO_2 (Figure 19) are displayed below.

Results and Discussion

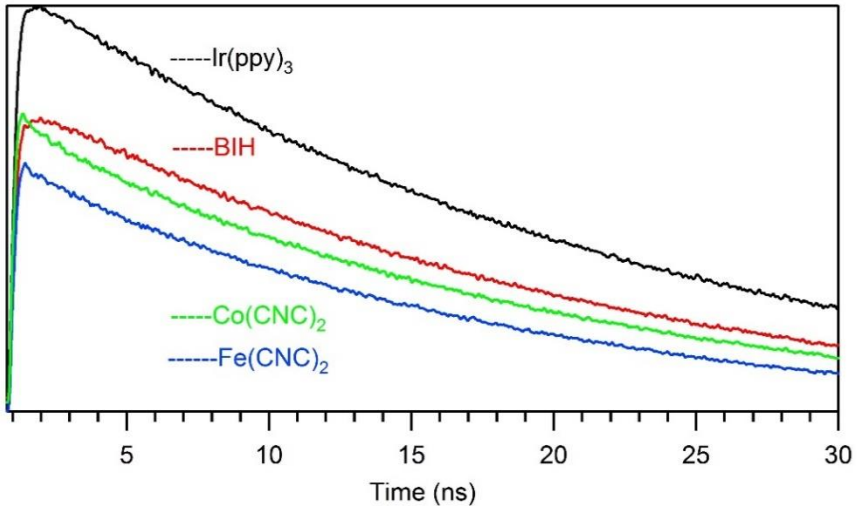

Figure 18: Fluorescent lifetimes of $Ir(ppy)_3$ under air.

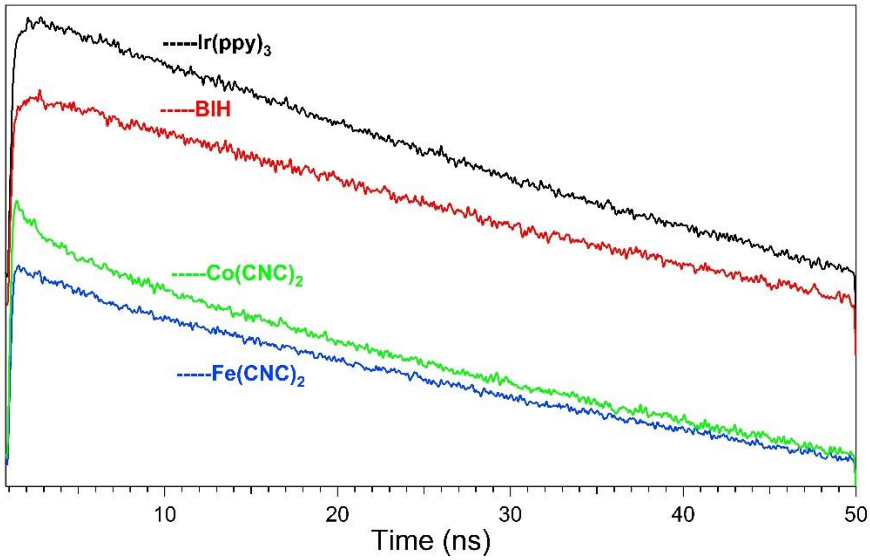

Figure 19: Fluorescent lifetimes of $Ir(ppy)_3$ under CO_2.

Table 3: Fluorescent lifetimes (ns) under air, N_2, and CO_2.

	$Ir(ppy)_3$	$Ir(ppy)_3$ + BIH	$Ir(ppy)_3$ + $Fe(CNC)_2$	$Ir(ppy)_3$ + $Co(CNC)_2$
Air	21.87	21.11	18.49	19.40
N_2	44.56	49.24	33.63	24.75
CO_2	133.46	139.85	73.69	56.75

As seen from the data in Table 3 the fluorescent lifetime increases with the change in the environment. Oxygen in the atmosphere usually has an inhibiting effect on the lifetime of molecules; however with a different environment the lifetime increases. CO_2 increases the lifetime more because it is a larger molecule than N_2.

c. BMMBBF

General structure, properties, applications

The next set of molecules to be discussed are the BisMethoxyMethylPhenyl BoraFluorenes or BMMBBF. Borafluorenes are molecules containing a boron atom covalently incorporated into p-conjugated molecular architectures. These materials have a number of interesting photophysical properties that make them ideal candidates for use as catalysts, OLED emitters, sensors, and electron transporters. The unique photophysical properties of the novel

borafluorene molecule (BMMBBF) were studied spectroscopically to better understand the frontier molecular orbitals. This molecule in particular has an unusual solution phase UV-vis absorption and emission spectrum. The solid state absorbance, emission, and fluorescence lifetime were studied in conjunction with Raman spectroscopy to better understand the photophysical properties of the solid.

Figure 20 illustrates the molecular structure of the BMMBBF molecule. The molecules studied here have the same BMMBBF base with an increasing number of thiophenes denoted by –MT, –BT, and –TT to study the effects of increasing the substituent length.

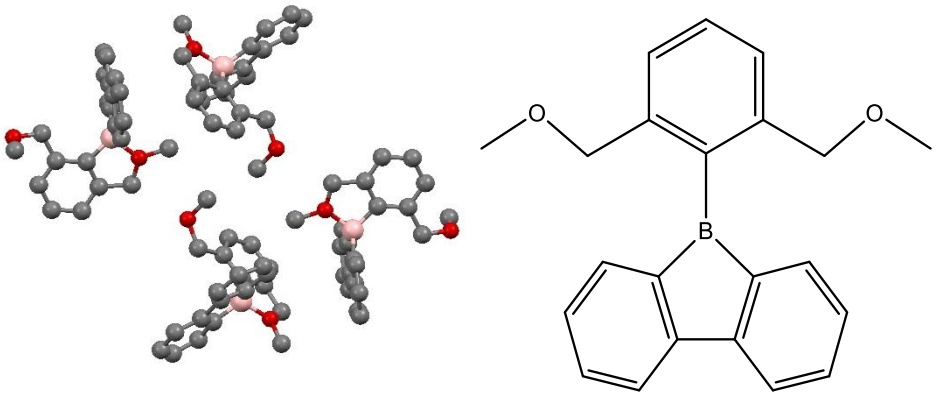

Figure 20: BMMBBF crystal structure (left) and molecular structure (right).

Experimental techniques and instruments

The molecules were dissolved in DCM, toluene, and tetrahydrofuran (THF) and were analyzed in the solid state (Figure 21). Absorption spectra were collected in the solid and solution state with the same instruments and methods previously mentioned. The same experimental set-up was used for emission analysis for the solid and solution state with an excitation wavelength of 405 nm with corresponding filter; emission was detected from 425 to 700 nm. The pulsed diode laser was used to collect the solution and solid fluorescent lifetimes at emission maxima of 500 and 625 nm. A Raman spectrum of the solution state in dry dichloromethane was collected at 633 nm.

Figure 21: BMMBBF substituent solutions in toluene and DCM; from left to right: –TT, –BT, and –MT. At left: solid crystals of the –TT, –BT, and –MT substituents from top to bottom.

Results and Discussion

The absorbance and emission spectra for the borafluorene base in DCM and as a solid (Figure 22) are provided below.

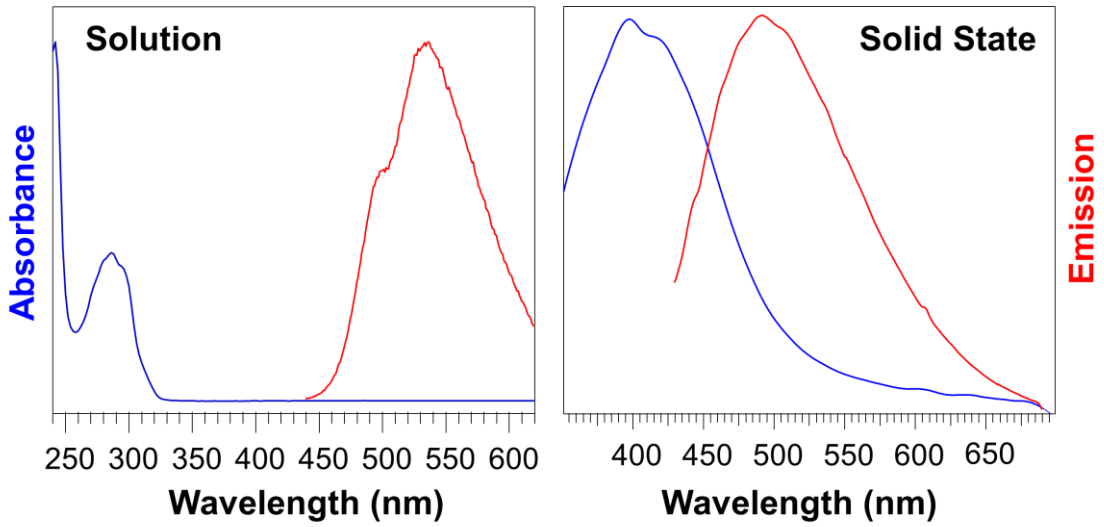

Figure 22: BMMBBF base absorbance (blue) and emission (red) spectra in DCM solution state and solid state.

In the solution state, the molecule only absorbs in the UV and emits in the visible. In the solid state, however, the absorbance maximum is around 400 nm and the emission maximum is around 500 nm. The fact that the photophysical properties in the solid are so different from the solution phase suggests that intermolecular interactions in the crystal structure play a significant role in determining the properties of the molecule.

The stark difference between absorption and emission spectra in solution compared to the solid state was explored by extending the conjugation thiophenes chain length. With the increase in number of thiophenes the absorption curve red shifted and the emission curve blue shifted to a midpoint between the maxima of about 450 nm. This shift mimics absorption and emission of the solid state. It is also observed that as the emission curve blue shifts the intensity of the curve at lower wavelength increases as the one at higher wavelength decreases in intensity. This is because the increase in substituent length has a strong influence on the LUMO (lowest unoccupied molecular orbital) levels and very little influence on the HOMO (highest occupied molecular orbital) levels.[16] These results are illustrated in the emission curves (Figure 23) for BMMBBF in DCM, toluene, and THF.

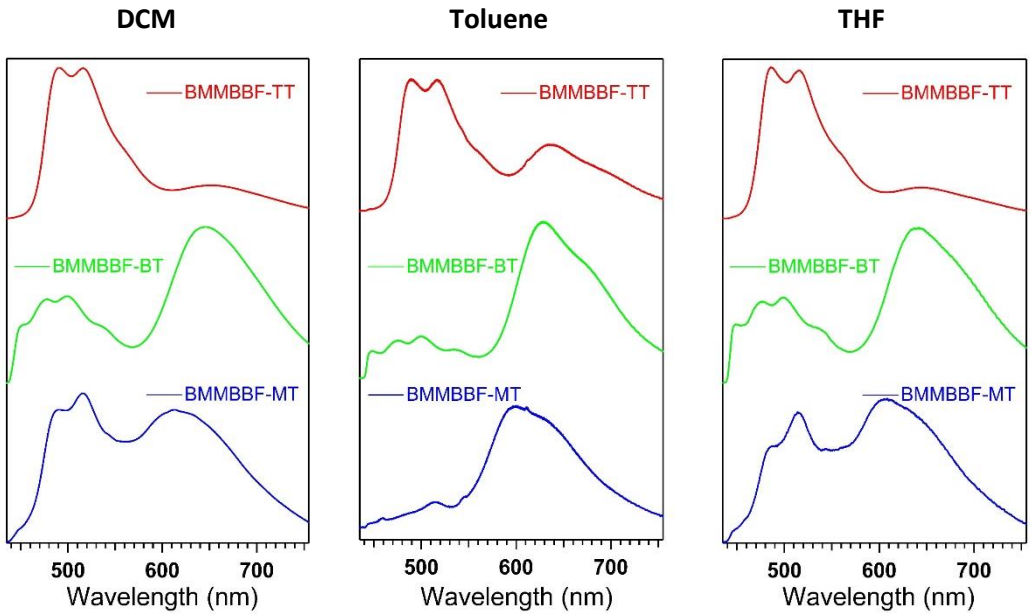

Figure 23: Emission spectra of BMMBBF conjugations in DCM, Toluene, and THF.

The lifetimes of the emission peaks at approximately 500 nm and 625 nm for each of the solutions were also found to examine the effect of extended conjugation chain on the excited state. The results are shown in Figure 24. The lifetimes are longer for all peaks at 625 nm with the

longest present in the –MT conjugation. This is because there are less thiophenes and the molecule can remain in the excited state more easily.

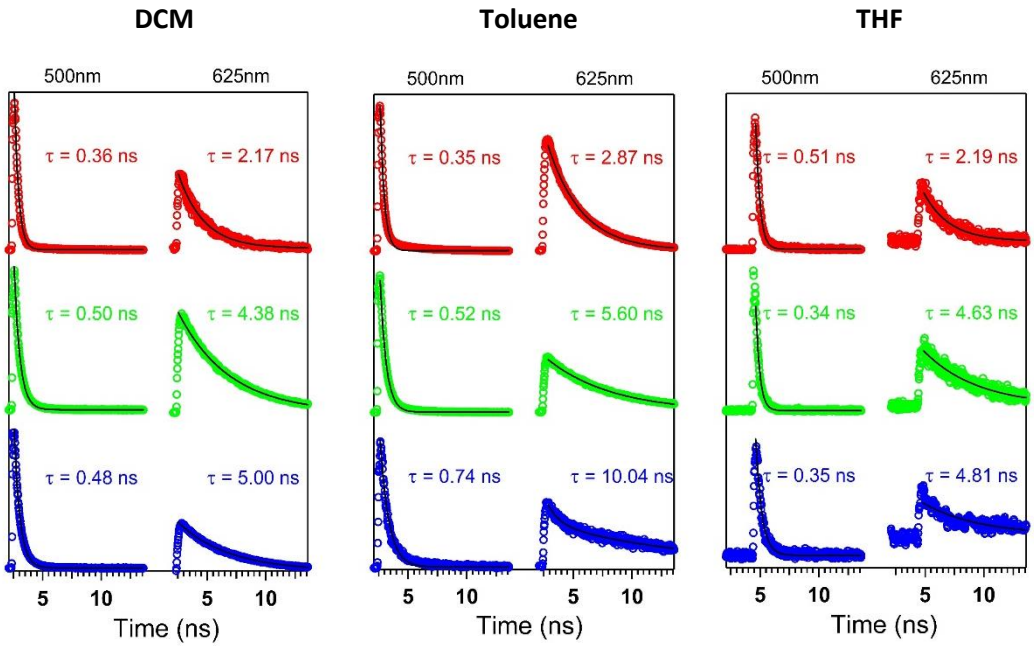

Figure 24: Fluorescent lifetimes of BMMBBF –MT(blue), –BT (green), and –TT(red) at 500 and 625 nm.

The Raman spectrum of the BMMBBF core is displayed in Figure 25.

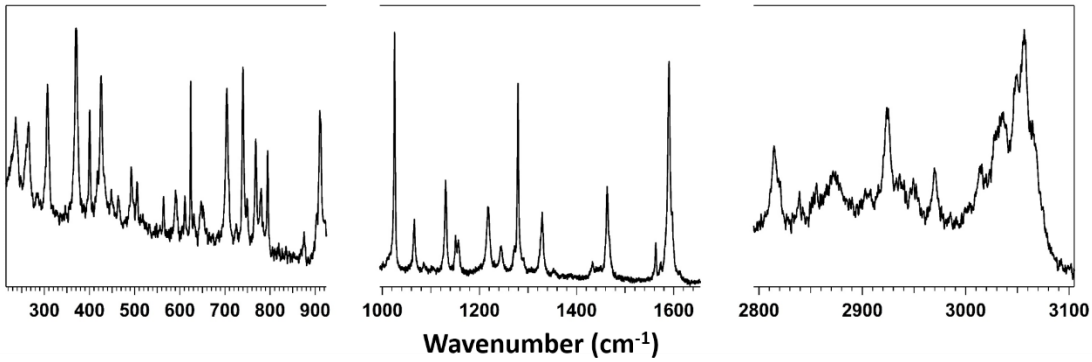

Figure 25: Raman spectrum of BMMBBF at 633 nm excitation wavelength.

Suitability for proposed application

From spectroscopic analysis it is evident that the borafluorene molecules possess photophysical characteristics suitable for use as OLEDs such as emission within the visible region and high fluorescent lifetimes. The –MT substituent in toluene provides the longest lifetime and

the most promise for potential application. With an increase in substituent length there is a decrease in lifetime along with a blue shift in the emission spectra. The most distinct emission peaks are seen in the THF solution.

3. CONCLUSION

The spectroscopic properties of newly synthesized materials were assessed and discussed in this thesis. The indolizine-squaraine based dyes synthesized for potential use as medical dyes were study in regard to absorption, emission, fluorescent lifetimes, stokes shift, quantum yield, molar absorptivity, and ATR-IR. The $Ir(ppy)_3$ molecules were studied to reveal the effects of gaseous environment on fluorescent lifetimes. Molecules for potential as OLEDs, namely BMMBBF, was studied in regard to absorbance, emittance, fluorescent lifetimes, and Raman spectroscopy. The spectroscopic properties from each of the molecule sets were revealed to be suitable for the molecules intended purpose.

From this project I gained a working knowledge on the general spectroscopic phenomena of emissive materials and how to assess these properties spectroscopically. Many experimental techniques and spectroscopic methods exist; thus one set of molecules could be studied for years and the results on the photophysical properties would not be exhaustive. However, from spectroscopic analysis the practical purpose of molecules can be determined and improved upon to provide a more immediate asset to society at large.

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